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„Umsetzung von Černý-Epoxiden mit Gilman-Cupraten. Neue chirale Bausteine für Naturstoffe polyketiden Ursprungs“

Abstract:

The use of carbohydrates as starting materials for the synthesis of natural products is a complementary method to asymmetric synthesis. Carbohydrates show defined chirality so that a “de novo” generation of chiral centres is not required. The supplement of chiral building blocks prepared from cheap sugars is ecologically and economically a challenging task.
In the first part of this dissertation the use of Palladium catalyzed allylic substitution on a carbohydrate backbone was demonstrated. The synthesis lead to an interesting chiral cyclopenten in high yield.
In the second part it was shown that 1,6-anhydrosugars are highly valuable starting materials for the preparation of chiral building blocks. 1,6-anhydrosugars can easily be prepared by pyrolysis of e.g. cellulose, starch or wood. During the work, a new reaction sequence was developed based on the opening of tosylated Černý-epoxides with cyano-Gilman cuprates. This new tandem epoxide allylalcohol rearrangement-cuprate cross coupling lead to a large number of new branched 1,6-anhydrosugar derivates. The products are stereochemically complementary to known Černý-epoxides derivatives, and may be useful as fragments for the synthesis of polyketide derived natural products (e.g. macrolides). In addition to the new tandem sequence other opening reactions of Černý-epoxides gave rise to a number of new compounds that may also prove to be useful as chiral building blocks. The reactions in this work mostly proceed in excellent yields and with high diastereoselectivity. For future work, the building blocks as well as the provided databases can be valuable for a chiral pool approach for the synthesis of natural and related products.